

SCIENCE FOR GLASS PRODUCTION

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STRUCTURAL CHANGES IN $R_2O - RO - TiO_2 - P_2O_5 - R_2O_3 - SiO_2$ GLASS DURING LIQUATION

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The mechanism of microliquation in $R_2O - RO - TiO_2 - P_2O_5 - R_2O_3 - SiO_2$ glasses is established. In these glasses, after heat treatment drop liquation leads to finely disperse volume sitalization of the crystalline component of the glass undergoing liquation. The formation of secondary spherical nonuniformities about 1 nm in size with drop-like formations intensifies the crystallization of glass after heat-treatment.

Key words: structure, drop microliquation, crystallization

An important problem in the production of finely disperse volume crystallized glasses is to establish the mechanism and kinetics of the initial stages of phase separation in them. It is known [1] that metastable liquation as an intermediate stage on the way to crystallization is energetically more favorable than stable crystallization, since the fluctuation nature of the micro-nonuniformities has a large effect on the separation of the glass during the precrystallization period [2]. The liquation mechanism of nucleation creates conditions for a uniform sitalized structure with formation of nano- and microsize crystalline phases, which largely determine the physicochemical and operational properties of crystallized glass materials.

Assuring microheterogeneity of the glasses by means of phase separation, the glass compositions are chosen on the corresponding phase diagrams in the region of existence of metastable liquation. It was established that the silicate systems $R_2O - RO - TiO_2 - P_2O_5 - R_2O_3 - SiO_2$ are characterized by quite wide regions of liquation. In general, the main reason for liquation in oxide systems is an electrostatic force interaction between the melt ions and the associated striving of the modifier cations and glass-forming cations to create an environment from oxygen anions in accordance with the coordination numbers. In addition, the stronger the field of the modifier cation, the stronger the tendency toward liquation is.

It is of special interest to study the particulars of liquation processes in calcium silico-phosphate glasses containing the cations Ti^{4+} and Zn^{2+} .

In titanium-containing glasses TiO_2 performs two functions depending on its structural role. For this reason, titanium whose cations will replace silicon in the structure of silicate glass determines its crystallization power, or its proneness to undergo separation [2].

Titanium ions, whose field strength is $Z_k/a^2 = 1.25(6)$ (according to Dietzel) and bond strength with oxygen Ti_4^{4+} 445(4), Ti_6^{4+} 306(6) kJ/mole, are compatible with the silico-oxygen network only to content $TiO_2 \approx 5\%$.³ For this reason, for high content of this oxide it can be supposed that wide regions of liquation exist in titanium-containing systems. The size of these regions as well as the intensity of the liquation processes depend on the type and number of alkali R_2O and alkali-earth metals RO , which determines the width of the region in the system $RO(R_2O) - TiO_2$.

Compared with magnesium and calcium ions, zinc ions are characterized by high field strength $Z_k/a^2 = 0.6(4)$, 0.52(6) and bond strength with oxygen 300(4) and 142(6) kJ/mole. For this reason, the region of glasses undergoing liquation is much wider in zinc-containing systems than in calcium- and magnesium-containing glasses [2].

An investigation of the mutual effect of ZnO and TiO_2 on phase separation in the system $SiO_2 - B_2O_3 - TiO_2 - ZnO - Na_2O$ established that for glasses in the spinodal region of liquation with 15 – 15% TiO_2 and 20 – 25% ZnO uniform finely disperse crystallization with crystallization of rutile predominating was observed [4].

A number of authors have studied liquation phenomena in zinc-containing silicate systems. Thus, D. F. Ushakov [5]

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³ Here and below, molar content.

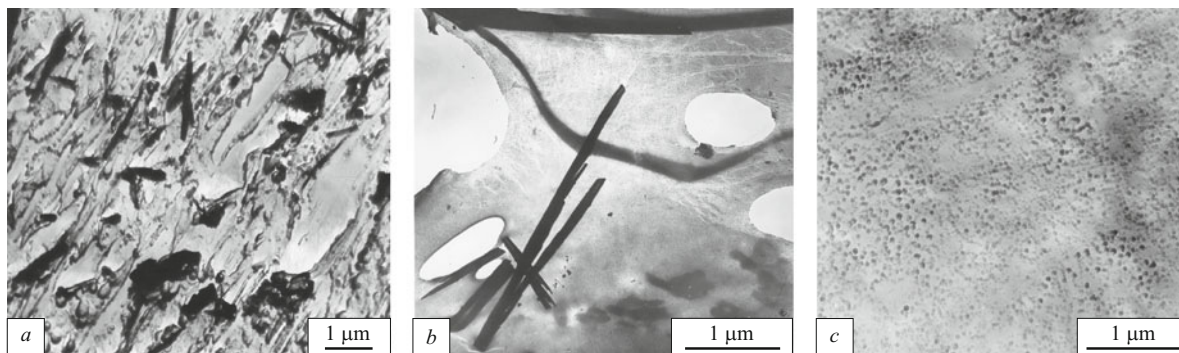


Fig. 1. Electronic photographs of 4-TsF glass.

explains the intensification of the initial glass in the system $R_2O - B_2O_3 - SiO_2$ where SiO_2 is replaced with ZnO and CaO by the presence of regions of immiscibility in the systems $ZnO - SiO_2$ and $CaO - SiO_2$, $CaO - B_2O_3$, and $ZnO - B_2O_3$. L. A. Bal'skaya and colleagues established [6] that in the system $SiO_2 - B_2O_3 - Al_2O_3 - ZnO - Na_2O$ intense interaction of Al_2O_3 and Na_2O results in mutual suppression of their homogenizing power with ratio $Al_2O_3/Na_2O = 1$. Localization of the sodium ions around the $[AlO_{4/2}]^-$ tetrahedra is the dominant factor which determines the liquation picture in the experimental system.

An important factor in studying the mechanism of phase separation in borosilicate glasses with ZnO and TiO_2 present simultaneously is the introduction of P_2O_5 into their composition. The idea of silicon and phosphorus-oxygen compounds being incompatible was used as a basis for developing fundamentally new crystalline glass materials with liquating structure [7]. It was established that the partial replacement of boron oxide by phosphorus oxide results in the boron-silicon tetrahedral element in the network being replaced by phosphorus-oxygen element with the simultaneous condensation of the groups $[BO_3]$. The increase of the acidity of the network as a result of phosphorus tetrahedra entering gives rise to active entry of modifiers into it and isolation of the borate component from it.

Investigations of the effect of the structure silico-phosphate glasses on its phase composition and the crystallization power established an inter-relation between the appearance of liquation in the glasses and the amount and ratio of $P_2O_5 - SiO_2$ on the mechanism of phase distribution and their crystallization power. The structure of the glass was studied using an IKS-14 spectrophotometer. To determine the mechanism of the liquation of glass after it is made the microstructure of the glass was studied under a Tesla electron microscope with initial magnification 2500 – 3000. The crystallization power was determined by a gradient-thermal method in the interval 500 – 900°C [9].

To study structure formation in the system $R_2O - RO - TiO_2 - P_2O_5 - R_2O_3 - SiO_2$, where $RO - CaO, ZnO, R_2O_3 - B_2O_3, Al_2O_3$, 10 compositions were synthesized in the region of calcium silico-phosphate glasses, which contained ZnO in amounts from 2 to 12%, and six compositions

of zinc silico-phosphate glasses with ZnO content 12 – 24% were synthesized. The $R_2O - RO - TiO_2 - P_2O_5 - R_2O_3 - SiO_2$ glasses are characterized by quite wide regions of phase separation. The liquation mechanism arising in the experimental glasses is due to the immiscibility of the multicomponent system indicated above in the binary subsystems $CaO - SiO_2$, $CaO - B_2O_3$, $P_2O_5 - SiO_2$, and $ZnO - SiO_2$, $ZnO - B_2O_3$.

To intensify the bactericidal effect due to the finely dispersed crystallization of calcium phosphates, 4 – 24% ZnO and 4 – 11% CaO were introduced into the experimental calcium silicophosphate glasses.

In the region of titanium-containing zinc phosphate glasses, because $ZnO/TiO_2 = 1.1 - 3.0$ conditions are created for crystallization of zinc titanates, which, as we have established previously, are responsible for their antibacterial properties. In these glasses, because of the increase in the ZnO content and the presence of boron oxide the zinc borate phase becomes isolated.

Calcium silicophosphate glasses 4-TsF, 6-TsF, and 10-1-TsF and zinc phosphate glass 20-TsF with different character of the structure and phase formation were chosen to study structure formation and the effect of liquid on the crystallization power of the model glasses.

The compatibility of titanium ions with the silicon-oxygen network is characteristic for glasses in the high-silica region 4-TsF and 6-TsF with ratio $Na_2O/TiO_2 > 1$ with TiO_2 content 5%. According to IR spectroscopy Ti^{4+} occupies tetrahedral positions. Zinc oxide in these glasses also enters into the structure of the glass and therefore fulfills the role of a structure former.

A further increase of the content of titanium oxide and zinc oxide to 10% in 10-1-TsF glass creates the conditions for a transition of the titanium cation into an octahedral position, since zinc is a definite kind of competitor for titanium on entry into the glass framework. In this glass, for the ratio $ZnO/TiO_2 = 1$ some Ti octahedra, remaining unbound in complexes of the type $[TiO_6/2]^{2-}M_2^+$ and $[TiO_4/2O]^{2-}M_2^+$, join along the edges. Such groupings are compatible with a titanosilicate network with the composition $ZnO - TiO_2 - SiO_2$ in limited quantities, just as with a silicon-oxygen network in $TiO_2 - SiO_2$ glasses. An increase in the number of

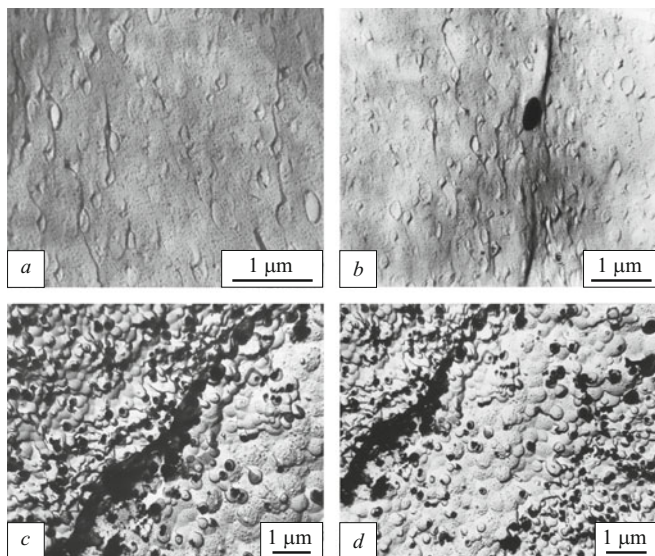


Fig. 2. Electronic photographs of 6-TsF glass.

these groupings results in liquation of the glass similarly to liquation of titanosilicate glasses.

In the inverted glass 20-TsF, which is characterized by the content $SiO_2 + B_2O_3 = 45\%$ and lower as compared with the glasses 4-TsF, 6-TsF, and 10-1-TsF by the amount of alkali oxides, the acidity of the glass matrix increases. As a result of an increase of the connectivity of the glass framework the number of regions saturated with titanium ions Ti^{4+} decreases, and the crystals of titanium-containing phases become larger. This results in precipitation of a titanium-containing phase during heat treatment with formation of a crystal glass structure. XPA confirms the presence of zinc titanates in the experimental glass. IR spectroscopy identified absorption peaks near 525 cm^{-1} , which belong to a TiO_6 octahedron and attest to the presence of titanates.

According to electronic microscopy the structure of the 4-TsF sample is microscopically nonuniform and volume crystallization is observed (Fig. 1a and b). After individual microparticles precipitate from the glass matrix, probably, of a crystalline character, plate-shaped and ellipsoidal nonuniformities with blurred contours are visible in it quite clearly, showing that the nonuniformities are covered with a thin layer of a glass phase. Needle-shaped particles $0.1 \times 2.3\text{ }\mu\text{m}$ in size with split ends are also visible (see Fig. 1b). The concentration of needle-shaped particles forms feathery regions, which according to XPA are hydroxyapatite crystals. Proof of the phase separation in this glass is the formation of a finely disperse phase on its surface; this phase consists of uniformly distributed nonuniformities of size about $0.03 - 0.05\text{ }\mu\text{m}$ and a band of homogeneous glass (Fig. 1c). Treating a fracture of this glass in HF established the presence of spherical nonuniformities, regions of a homogeneous character, and specific needle-shaped particles of size $0.15 \times 1.6\text{ }\mu\text{m}$ and $0.18 - 0.22\text{ }\mu\text{m}$ (see Fig. 1a).

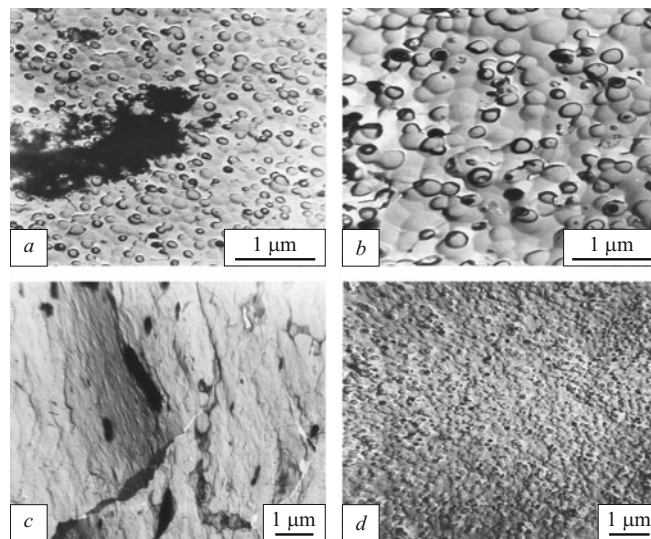


Fig. 3. Electronic photographs of 10-1-TsF glass.

The glass 6-TsF is a multiphase system, which consists of a glass matrix and drop-shaped formations which differ in number and size and which are centers of crystallization (Fig. 2a and b). Treating a fracture of 6-TsF glass in HF showed the presence of secondary spherical nonuniformities ranging in size from 0.0018 to $0.003\text{ }\mu\text{m}$, which precipitate on drop-shaped particles (Fig. 2c and d); this could attest to internal liquation followed by ordering of the structure. A $3\text{ }\mu\text{m}$ band similar to double nonuniformities borders a band which is represented by clusters of a large number of nonuniformities smaller than $0.028 - 0.3\text{ }\mu\text{m}$. This shows that several regions of immiscibility are present in the glass. The surface of 6-TsF glass is also characterized by the presence of drop-shaped particles $0.08 - 0.3\text{ }\mu\text{m}$ in size (pitted particle $0.2 - 0.4\text{ }\mu\text{m}$ in size) (see Fig. 2a) and uniform distribution of spherical nonuniformities $0.002 - 0.003\text{ }\mu\text{m}$ in size (see Fig. 2b). Short microcracks were observed around drop-shaped formations. It is evident on the photomicrograph of the fracture that a microcrack forms behind each individual particle. Taken as a whole this represents a characteristic picture: microcracks emanate parallel to one another from all particles in the direction of the crystallization front. This made it possible to establish in the structure of the experimental glass the presence of a large number of regions which differ with respect to structure or composition from the glass matrix in cases where these regions — the initial stages of nucleation of crystalline phases — lie beyond the limits of capability of the method of investigation. For this reason, the fluctuation nature of the micrononuniformities can be judged according to the appearance of parallel cracks on the fracture surface.

The microstructure of the surface of a 10-1-TsF sample is distinguished by the nonuniform character of the distribution of distinct drop-shaped particles ranging in size from 0.5 to $1\text{ }\mu\text{m}$ and the presence of individual sections of spherical micrononuniformities (Fig. 3a and b). The particle singled

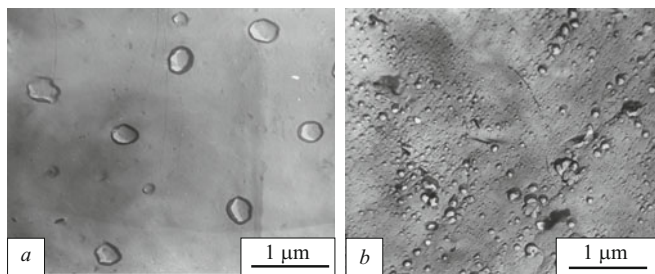


Fig. 4. Electronic photographs of 20-TsF glass.

out in Fig. 3a has a feathery structure of hydroxyapatite. Treatment of the glass sample in HF made it possible to observe on its fracture uniformly distributed particles about $0.09 - 0.17 \mu\text{m}$ in size (Fig. 3c) and secondary formations $0.001 \mu\text{m}$ in size in their boundaries (Fig. 3b and d). Needle-shaped particle $> 1 \mu\text{m}$ in size and spherical formations about $1 \mu\text{m}$ in size were also observed in the fracture of the sample.

Separate, distinct, isolated, closed drops with a uniform distribution in the matrix are observed in the electron-microscope photographs of the surface of 20-TsF glass (Fig. 4a). The microstructure of this glass on the fracture is characterized by a large number of spherical formations ranging in size from $0.047 - 0.08$ to $0.001 \mu\text{m}$ (Fig. 4b) and $0.5 \mu\text{m}$ drop-shaped embryos oriented in a definite direction. Spherical embryos are of a fluctuation nature and are nucleators, which gives rise to the formation of finely disperse phases during heat treatment. Gradient-thermal studies show that a negligible number of isolated drop-shaped embryos in this glass are characterized by a homogenous structure, which remains even after heat-treatment.

In general, as the zinc oxide content in the experimental glasses increases, the size of the secondary spherical micro-nonuniformities within the drop-shaped formations decreases from 0.03 to $0.05 \mu\text{m}$ for 4-TsF and to $0.001 \mu\text{m}$ for 20-TsF, which is probably due to the corresponding increase of zinc oxide in them.

The results of the determination of the crystallization power of all experimental glasses by the gradient-thermal method show that they are characterized by macroliquation separation heat-treatment with difference content of liquating phases. The amount of opaque and transparent phases in the experimental glasses is determined by, first and foremost, the content of ZnO and TiO_2 and their ratio. In glasses with ZnO content 4 and 6%, more intense crystallization was observed at the initial stages of heat treatment. After heat treatment, an increase of the transparent phase is observed in these glasses and, as a result, general opalescence of these glasses occurs at $720 - 900^\circ\text{C}$. For the glass 10-1-TsF, as the titanium oxide content increases from 10% and $\text{ZnO}/\text{TiO}_2 \approx 1$ intense crystallization occurs in the temperature range $620 - 780^\circ\text{C}$, which results after heat treatment in a higher content of the obviously crystalline phase as compared with the transparent phase. An increase of the ZnO content to 20% for the 20-TsF

glass with ratio $\text{ZnO}/\text{TiO}_2 > 2$ gives rise to an increase and isolation of a negligible quantity of the transparent phase from the crystalline phase after heat treatment.

CONCLUSION

A mechanism of microliquation in glasses in the system $\text{R}_2\text{O} - \text{RO} - \text{TiO}_2 - \text{P}_2\text{O}_5 - \text{R}_2\text{O}_3 - \text{SiO}_2$ is established. It is shown that in $\text{R}_2\text{O} - \text{RO} - \text{TiO}_2 - \text{P}_2\text{O}_5 - \text{R}_2\text{O}_3 - \text{SiO}_2$ glasses droplet liquation results in finely disperse volume sitallization of the crystalline component of the liquating glass after heat treatment. The amount of the transparent phase in the experimental glasses after heat treatment is determined by the character of the crystallization processes and the separation at the initial stages. In glasses with intense crystallization at temperatures to 780°C the content of the transparent phase after heat treatment increases. In glasses with TiO_2 content from 8 to 10% the formation of the secondary spherical nonuniformities about 1 nm in size within the drop-shaped formations leads to intensification of the crystallization of the glass after heat treatment. An increase of the ZnO content to 20% gives a negligible increase of the quantity and isolation of the transparent phase after heat treatment.

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